

Remarks

This Application has been carefully reviewed in light of the Office Action mailed February 24, 2006. In the Office Action, claims 1-11, 13, 14 and 26-30 were rejected. By this paper, Applicant has amended claims 1, 3, 5-8, 10, 11, 14 and 26-30 and has cancelled claims 2 and 4 to clarify the subject matter in which the Applicant claims as its invention and to advance prosecution of this case. No new matter has been introduced by this Amendment. Applicant does not admit that the Amendment was necessary as the result of any cited art or Examiner objections or rejections. Applicant respectfully requests reconsideration of the above-identified application in view of the following remarks.

Claims 1-11, 13, 14 and 26 were rejected as being unpatentable over *Schneider* (U.S. Patent No. 3,415,364) in view of *Helsemans et al.* (U.S. Patent No. 5,418,261) and *Rosthauser* (U.S. Patent No. 6,224,800 B1).

According to the Examiner, *Schneider* discloses a protective packaging for protecting an article comprised of a polyurethane foam structure conforming to a portion of the article for protecting the article. The Examiner admits that *Schneider* fails to disclose a foam comprising a shape memory foam which is crosslinked. The Examiner attempts to cure this defect by combining the *Helsemans et al.* teachings with the *Schneider* teachings. The Examiner opines that *Helsemans et al.* discloses a polyurethane foam for packaging which is a shape memory foam and which is crosslinked for the purpose of obtaining lightweight packaging. The Examiner combines the reference based on the motivation that one of ordinary skill in the art would have recognized the advantage of providing for the polyurethane foam of *Helsemans et al.* in *Schneider*, which comprises packaging, depending on the desired lightweightness of the end product. The Examiner admits that *Helsemans et al.* does not disclose a hydrophobic foam. The Examiner attempts to cure this defect by combining the *Rosthauser* teachings with the combined teachings of *Helsemans et al.* and *Schneider*. According to the Examiner, *Rosthauser* teaches that isocyanates comprising diphenylmethane

diisocyanate are hydrophobic, and such isocyanates are disclosed by *Helsemans et al.*, and therefore, the *Helsemans et al.* foam is at least partially hydrophobic.

Applicant respectfully traverses this rejection because the proposed combination, assuming that the references are properly combinable, does not teach, disclose, or suggest the claimed invention. Moreover, the Examiner has not and cannot show the requisite motivation to combine the references.

For instance, the proposed combination does not teach, disclose or suggest a hydrophobic, polyurethane SMF structure with the shape memory characteristic, as recited in claims 1, 3, 5-11, 13, 14 and 26. *Helsemans et al.* discloses hydrophilic foams. *Helsemans et al.* discloses a polyurethane crosslinked shape memory foam based on polyisocyanate and polyols, wherein the polyols have hydroxyl functionality from 2.2 to 6 and with average oxyethylene content of at least 86% by weight. (col. 5, ll. 47-49.) Polyurethane shape memory foams according to the *Helsemans et al.* invention are hydrophilic due to the polyol composition requiring an average oxyethylene content of at least 86% by weight.

The following references¹ support that polyurethanes, prepared from isocyanates and polyols, based on polyols with oxyethylene content are hydrophilic. Saunders and Frisch reported that polyurethane sponges can be manufactured using ethylene oxide modified polyethers and polyoxyethylene polyols (glycols), which are also described as polyethylene glycols. "Greater water absorption can be obtained by including a more hydrophilic hydroxyl component in the formulation, such as ethylene oxide modified polyethers." (J.H. Saunders and K.C. Frisch, "Polyurethanes Chemistry and Technology, Part II," Interscience Publishers, John Wiley & Sons, New York, 1964, pp. 173 and 182). The hydrophilic character of polyethylene glycols is also recorded by Gunter Oertel. (Oertel, Gunter, Polyurethane Handbook, Hanser Publishers, New York, 1985, p. 44).

¹ The references cited in this response are attached as an Exhibit so that the Examiner can refer to the references while considering the Applicant's remarks.

Moreover, Lamba et al. provides that “[p]olyethylene oxide-based materials swell in water due to the hydrophilic nature of the soft segment.” (Lamba et al., “Polyurethanes in Biomedical Applications,” CRC Press, New York, 1998, p. 15). In polyurethane chemistry, soft segments are comprised of polyols. Therefore, according to Lamba et al., it is the polyol that controls the water affinity of polyurethanes, not the isocyanate. Frisch provides that poly(oxyethylene) glycols (PEGs) are used for the production of hydrophilic urethane polymers, including foams. Frisch reports that if hydrophobic properties of urethane applications are desirable, propylene oxide is often used alone in synthesis of polyoxyalkylene polyols or in combination with ethylene oxide, generally less than 15% of ethylene oxide. (Frisch, “High-Performance Polyurethanes” in “Macromolecular Design of Polymeric Materials,” Editors Hatada et al., Marcel Dekker, Inc., New York, 1997, p. 529). Therefore, the foams provided by *Helsmans et al.*, which have a polyol content that is on average at least 86% oxyethylene, are hydrophilic. Conversely, Applicant’s claimed invention is drawn to polyurethane shape memory foams that are hydrophobic. The hydrophobic nature of the Applicant’s claimed foams allow them to be used in many applications where hydrophilic foams are unsuitable.

The *Rosthauser* reference does not cure the defects in the teachings of the proposed combination of *Helsemans et al.* and *Schneider*. *Rosthauser* teaches that diphenylmethane diisocyanates as a binder can be added to produce polyureas – not polyurethanes. (col. 2, ll. 61-62). Applicant’s claims recite a polyurethane SMF structure. Not only does the proposed combination including *Rosthauser* fail to teach, disclose or suggest the claimed invention, but it is also inappropriate to combine *Rosthauser* with *Helsemans et al.* and *Schneider* because *Rosthauser* is directed at a completely different class of materials, i.e. polyureas, than the *Helsemans et al.* and *Schneider* references, which are directed at polyurethanes.

Rosthauser provides that “the binder may be a hydrophobic isocyanate such as any of the polymeric diphenylmethane diisocyanates” (col. 2, ll. 61-62). *Rosthauser* also discloses that “the catalyst is included to ensure that the isocyanate/water reaction is not slowed

to such an extent that the pressing time necessary to produce the molding product is significantly increased.” (col. 2, ll. 66-67, and col. 3, ll. 1-2). The reaction of isocyanate binder with water results in a polyurea. Therefore, *Rosthauser* describes formation of a polyurea, which is a different class of materials than polyurethanes described by *Helsemans et al.* and *Schneider*. For at least this reason, the requisite motivation does not exist to combine the *Rosthauser* reference with the *Helsemans et al.* and *Schneider* references.

Moreover, polyureas formed in the reaction described by *Rosthauser* do not contain any polyol segments (also known as soft segments), which controls the properties of polyurethane and polyurethane foams and their affinity towards water, as supported by the above-identified references cited by the Applicant. As an example, *Lamba et. al.* states that “polyethylene oxide-based materials swell in water due to the hydrophilic nature of the soft segments.” (p. 15). *Lamba et al.* also provides that the nature of the polyol affects other properties of polyurethanes, such as the environmental (hydrolytic) stability of the polyurethanes: “[p]olyalkyl glycols offer an alternative to the relatively less stable polyether and polyester polyurethanes. Hydrogenated polybutadiene polyisobutylene-based polyurethanes show excellent resistance to light and thermal degradation and hydrolysis.” *Id.* “Polypropylene oxide-based polyurethanes offer greater hydrolytic resistance.” *Id.* Therefore, the properties of polyurethane are determined by the nature of the polyol, i.e. soft segment, not the isocyanate, and thereby polyurethane shape-memory foams described by *Helsemans et al.* will be hydrophilic due to the nature of the polyols that required greater than 86% by weight content of oxyalkylene segments.

For at least the reasons set forth above, claims 1, 3, 5-11, 13, 14 and 26 are patentable over the proposed combination and the other art of record.

Claims 27 and 28 were rejected under 35 U.S.C. § 103(a) as being unpatentable over *Schneider* in view of *Helsemans et al.*, and further in view of *Hayashi et al.* (U.S. Patent No. 5,049,591). The Examiner admits that *Schneider*, *Helsemans et al.* and *Rosthauser* fail to disclose a shape-memory foam based on an aromatic polyester polyol reacted with an

isocyanate. The Examiner attempts to cure this defect by combining the teachings of *Hayashi et al.* with the teachings of *Schneider, Helsemans et al.* and *Rosthauser*. Applicant respectfully traverses this rejection because the proposed combination, assuming that the references are properly combinable, does not teach, disclose, or suggest the claimed invention.

For instance, the proposed combination does not teach, disclose or suggest a crosslinked SMF structure based on aromatic polyester polyols, as recited in pending claims 27 and 28. The Examiner admits that *Schneider, Helsemans et al.* and *Rosthauser* fail to disclose a shape-memory foam based on an aromatic polyester polyol reacted with an isocyanate. *Hayashi et al.* fails to cure this defect. Further, pending claims 27 and 28 recited a crosslinked SMF, which is not taught, disclosed or suggested by *Hayashi et al.* *Hayashi et al.* provides a shape-memory foam composed of a difunctional diisocyanate, a difunctional polyol, and a difunctional chain extender containing active hydrogen (col. 2, ll. 22-26). The difunctional nature of all components used in preparation of the shape-memory foams ensure that the resulting structure is thermoplastic, without any crosslinks. To support preparation of a thermoplastic foam, *Hayashi et al.* show that the difunctional polyols are represented by the general formula OH-R'-OH (col. 2, ll. 60-63). Furthermore, to ensure that no crosslinking has occurred, *Hayashi et al.* states "[t]he polyurethane foam is made up of polymer chains having substantially no excess isocyanate groups at their terminals and hence contains no allophonate links which form rigid crosslinks." (col. 2, ll. 34-39). Furthermore, *Hayashi et al.* states that "this means that the polyurethane foam is a thermoplastic chain polymer which can be processed upon heating." (col. 2, ll. 34-39). Crosslinked polyurethanes can not be processed upon heating. The teachings of *Hayashi et al.* are limited to a thermoplastic structure. Contrarily, claims 27 and 28 recite a crosslinked SMF composition based on aromatic polyester polyols. For at least this reason, claims 27 and 28 are patentable over the proposed combination and the other art of record.

Claims 29 and 30 are further rejected under 35 U.S.C. § 103(a) as being unpatentable over *Schneider* in view of *Helsemans et al.* and *Rosthauser*, and further in view of *Chaffanjon et al.* (U.S. Patent No. 5,594,097). The Examiner admits that *Schneider*,

Helsemans et al. and *Rosthauser* fail to disclose a shape-memory foam based on polycarbonate polyol reacted with an isocyanate. The Examiner attempts to cure this defect by combining the teachings of *Chaffanjon et al.* with the teachings of *Schneider*, *Helsemans et al.* and *Rosthauser*. Applicant respectfully traverses this rejection because the proposed combination, assuming that they are properly combinable, does not teach, disclose, or suggest the claimed invention. Moreover, the Examiner has not and cannot show the requisite motivation to combine the references.

For instance, the proposed combination does not teach, disclose or suggest a SMF composition having a shape memory characteristic based on polycarbonate polyols, as recited in claims 29 and 30. *Chaffanjon et al.* provides a polyol and a process for preparing a flexible polyurethane foam, from a specific class of polyols (col. 1, ll. 10-12). *Chaffanjon et al.* provides that flexible polyurethane foams refers to cellular product which exhibits substantial shape recovery after deformation (col. 3, ll. 13-15). *Chaffanjon et al.* does not teach or suggest the claimed shape memory characteristic, i.e. that the foam can be compressed and when cooled below the T_g , that retains the compressed shape without any aid from an outside force, and that regains substantially its original shape after heating to above the T_g . Contrarily, claims 29 and 30 recite a SMF composition having a shape memory characteristic based on polycarbonate polyols. For at least this reason, claims 29 and 30 are patentable over the proposed combination and the other art of record.

Furthermore, the Examiner has not shown and cannot show the requisite motivation to combine the teachings of *Chaffanjon et al.* with the teachings of *Schneider*, *Helsemans et al.* and *Rosthauser*. *Chaffanjon et al.* states “[s]uprisingly it has been found that by using a special polyol under special conditions the processing and the properties of flexible polyurethane foams may be further improved.” (col. 1, ll. 16-19). The specific class of polyols according to the *Chaffanjon et al.* are “also polyhydroxyl derivatives modified by vinylpolymerisation, such as for example obtained by polymerizing styrene and acrylonitrile in the presence of polyether polyols or polycarbonate polyols.” (col. 5, ll. 44-47). Therefore, only in the preparation of this special class of polyols, polyether polyols and polycarbonate

polyols may be interchangeable. The basis of the Examiner's motivation that *Chaffanjon et al.* teaches the interchangeable use of any polyether polyol and polycarbonate polyol is flawed. For at least this reason, claims 29 and 30 are patentable over the proposed combination and the other art of record.

Further, the Examiner has not shown and cannot show the requisite motivation to combine the teachings of *Rosthauser* with the teachings of *Schneider*, *Helsemans et al.* and *Chaffanjon et al.* Moreover, *Rosthauser* does not teach the claimed subject matter lacking from *Schneider*, *Helsemans et al.* and *Chaffanjon et al.* *Rosthauser* teaches that diphenylmethane diisocyanates as a binder can be added to produce polyureas – not polyurethanes. (col. 2, ll. 61-62). Applicant's claims 29 and 30 recite a SMF structure produced by reacting an isocyanate and a polycarbonate polyol, i.e. a polyurethane. Not only does the proposed combination including *Rosthauser* fail to teach, disclose or suggest the claimed invention, but it is also inappropriate to combine *Rosthauser* with *Helsemans et al.* and *Schneider* because *Rosthauser* is directed at a completely different class of materials, i.e. polyureas, than the *Helsemans et al.* and *Schneider* references, which are directed at polyurethanes.

CONCLUSION

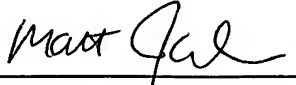
The present amendments were not earlier presented because the amendments and remarks submitted with the prior amendment addressed all stated rejections in the Office Action. The present amendments and remarks are directed at further illustrating the patentability of the Applicant's claimed SMF structures. The Examiner has already conducted a search on these concepts since it was recited in the original claims. Therefore, the present claims do not raise any new issues for search or consideration and do not require any further searching by the Examiner. As such, Applicant submits that the amendment is appropriate for entry, and that the claims are in a condition for allowance, which action is respectfully requested.

No additional fee is believed to be due as the result of the filing of this paper. However, any additional fees or credits should be applied to Deposit Account 02-3978. A duplicate of this paper is enclosed for that purpose.

If the Examiner feels that a telephone conference would advance prosecution of this Application in any manner, the Examiner is invited to contact Matthew M. Jakubowski, Attorney for Applicant, at Examiner's convenience at (248) 358-4400.

Respectfully submitted,

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VOLUME XVI

Part II

POLYURETHANES CHEMISTRY AND TECHNOLOGY

Part II. Technology

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P R E F A C E

Part I of "Polyurethanes" dealt with the basic aspects of the chemistry of isocyanates and polyurethanes. In addition, some of the fundamental principles underlying the formation of urethane foams, elastomers and coatings were presented, and correlations between the chemical structure and the physical properties of these polymers were made.

Part II covers the rapidly expanding technology of polyurethanes. This major commercial class of polymers has grown from the early discoveries of Professor Otto Bayer and co-workers at I. G. Farbenindustrie, and their many subsequent developments at Farbenfabriken Bayer. In a relatively short time span polyurethane production in the United States has grown from 35 million pounds in 1958 to about 225 million pounds in 1963. Flexible urethane foams have paced the growth of this most versatile class of polymers. Recently, rigid foams have been giving indications that their long heralded growth may become a reality rather than a gleam in the eyes of optimistic market forecasters. Urethane coatings and elastomers are also showing encouraging growth patterns. How fast a special area of urethane technology may experience growth is witnessed by the spectacular advent of the elastic "spandex" fibers, which by definition are composed of at least 85% segmented urethane fibers. Virtually unknown a few years ago, spandex fibers are expected to capture over half of the total elastic fiber market within the next few years and are slated to go into many new applications such as sportswear, dresses, and upholstery materials.

Other fields of polyurethane technology, though subjects of intense research efforts, are either in an early stage of commercial development or are still awaiting "break throughs" by diligent research workers.

The various areas of urethane technology in Part II have been treated in an extensive manner to provide a thorough coverage of early developments, as well as those systems which are currently of greatest importance. It is realized that urethane technology is a

for sound insulation and be used to seal seams on air-conditioning ducts (116,118,120).

6. Carpet Underlay

The trend toward larger carpeted areas and wall-to-wall covering encourages the use of rug underlayment for which flexible urethane foam is suitable. The foam provides cushioning, is nonskidding and does not mat down. It also imparts a luxurious feel even to less costly carpeting. So far most of the flexible foam underlay was supplied in form of thin sheets. However, more recently, improved techniques of laminating to fabrics (see Section VI, 5, on Clothing, Textile, and Foam Laminates) permit the direct bonding of foam to carpeting where it also acts as a base for supporting carpet pile (34,133).

Carpet underlay made from flexible urethane foam has not reached as yet its full potential. The key to accelerated growth of urethane foams in this application appears to be the continued development of suitable methods and equipment for directly applying the foam to the rug backing during the manufacturing operation. Of course the trend toward lower finished costs for foams will improve its competitive position with low-cost hair and felt products which are currently the most widely used materials for rug underlay (116,120).

7. Sporting Goods

There is a great variety of applications for flexible foam in the sporting goods field although many of these consist of relatively small volume items, making use of the shock-absorbing qualities of urethane foam. Typical applications include protective headgear liners for football, hockey, racing, lacrosse and polo; boxing and baseball gloves; gymnasium mats and protective devices such as knee, hip, and shoulder pads, nose guards, and athletic supporters (126). Other sport items made of urethane foam are durable fishing floats, gun stock pads to absorb recoils, casting rod handles, golf club grips, marine life preservers, and sleeping bags. A various assortment of beach items ranging from floats, beach, and pool pads to beach wear are made from flexible foam (49a,126).

8. Toys and Novelties

Assorted shapes can be die-cut from slab stock scrap, using conventional machinery for toys and novelties (126). Both polyester and polyether urethane foams are employed for this use. A variety of molded toys and novelties are also produced from urethane foam.

Toy manufacturers are rapidly turning to the use of urethane foam in place of the traditional sawdust and cotton stuffing for stuffed toys. Generally, foam scrap is being widely employed for these applications (110,144). A distinct advantage of urethane toys is their ability to be laundered.

Thiokol Corp. has developed foams based on two types of hydrophilic polyesters which can be used for toys that swell in water (116).

Novelty items of all sorts are made of flexible foam such as marine life replicas ranging from sharks and starfish to sea anemones which were molded for Pacific Ocean Park's "Neptune's Kingdom" (49).

Brethane foam can be readily colored by adding special pigments either in form of water dispersed or oil dispersed pigments, which is of particular importance for many toy and novelty uses such as dolls, various types of slippers, glass coasters, etc. (47).

9. Sponges and Miscellaneous Household Items

Flexible urethane foam has made a noticeable penetration in commonly used household goods. Foremost among these are the urethane sponges which are outstanding in their resistance to abrasion, chemicals, acids, and solvents (49). The water absorption of these sponges is generally low compared to natural or cellulosic sponges, primarily due to the hydrophobic nature of the urethane polymers. However, greater water absorption can be obtained by including a more hydrophilic hydroxy component in the formulation, such as ethylene oxide modified polyethers. The retail sale of urethane sponges in 1961 was estimated at over \$10 million (120). Unlike conventional sponges, the urethane products can be produced in a wide range of densities and cell sizes. They can be impregnated with various liquid detergents and can be readily laminated to other materials. Currently, polyester-based products make up a great percentage of miscellaneous urethane foam household items which include bath and household sponges, clothes and floor brushes, dish and floor mops.

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The various areas of urethane technology in Part II have been treated in an extensive manner to provide a thorough coverage of early developments, as well as those systems which are currently of greatest importance. It is realized that urethane technology is a

Urethane foams resistant to fungi and bacteria were produced by incorporation of 0.2 to 5% by weight of the foam of a tetraalkyl thiuram disulfide or a dialkyl dithiocarbamate (56). The thiuram or the dithiocarbamate was added either prior to foaming or by treating the foam with solutions of these compounds.

The formation of elastomeric urethane sponge was reported by Hill (80) who reacted adducts of polyalkylene ether glycols and TDI with water. A typical preparation consisted of reacting 120 parts poly(oxyethylene) glycol of approx. 4000 M.W. with 40 parts TDI at 70°C. for 4 hr. The resulting viscous liquid on cooling to room temperature became a pale yellow-brown wax. Upon dissolving 50 parts of this wax in 150 parts water at 35°C., foaming occurred within 1 min. and frothing of the solution yielded a spongy mass. Similar spongy materials were formed when TDI was replaced by phenylene diisocyanate or MDI.

Hydrophilic urethane foams suitable for sponges were reported by Elkin (55). A polyester mix prepared from triethylene glycol and adipic acid and ethylene glycol and adipic acid was blended with polyethylene glycol of 1000 M.W. and reacted with TDI. The resulting prepolymers were foamed employing 2-pyrrolidone as catalyst, yielding foams of varying density, hardness, tensile strength, and water absorbency by adjusting the free NCO content, the proportion of polyester to polyglycol and the composition of the polyester.

Hydrophilic foams have also been prepared by impregnating foams with hydrophilic materials such as hydroxyethyl cellulose (150).

The use of lecithin in the preparation of flexible urethane foams was disclosed by Schmidt and Braun (172). The resulting foams exhibited a cellular structure resembling that of a natural sponge.

The incorporation of flexible or rigid urethane foam in the voids between the flutes of corrugated paperboard was described by Rodgers (154). The foam imparted to the board superior dry strength, greatly superior resistance to crushing, and top load at high humidities, as compared with untreated corrugated board. It also provided an insulation barrier and effective cushioning against repeated impact. A board treated with foam made from castor oil (85 parts), polyethylene glycol 200 (15 parts), and TDI (100 parts), and employing diethylethanamine hydrochloride as catalyst, was 190-250% more crush-resistant than the untreated board, depending upon the relative humidity. It also exhibited greater resiliency and

returned to its original thickness after exposure to 95% relative humidity while the untreated board under similar conditions was irreparably damaged.

Flexible foams made from polyvinyl chloride, a plasticizer (e.g., tritolyl phosphate), phenyl isocyanate, and azodiisobutyronitrile, were described by Carpenter (30). After mixing the components on a mill, the mixture was placed in a mold and heated to 150°C. for 5 min., and maintained at this temperature for 7 min. It was then cooled to 20°C., removed from the mold, and after relaxing for 24 hr., heated in an oven at 110° for 8 min. and cooled. The initial cellular material was placed for 72 hr. in an atmosphere saturated with water vapor at 40-45°C., causing liberation of carbon dioxide and further expansion of the foam.

Nonflammable elastic foams with slow recovery were prepared by reaction of a polyester with an isocyanate in the presence of a vinyl plastisol (185). A 20-lb./ft.³ foam was made by addition of 28 parts 2,4-TDI to a mixture of 120 parts polyvinyl chloride, 80 parts tolylphosphate, 5 parts Ba-Cd laurate, 18 parts polyester, and 1.4 parts water.

Flexible thiourethane foams were prepared by the reaction of water with a condensation product of a diisocyanate and a liquid polysulfide polymer containing terminal sulphydryl groups. The latter had a molecular weight of about 1000 to 4000 and possessed polysulfide linkages connecting recurring units consisting of alkylene or oxyalkylene units (101). The polysulfide employed was a linear polymer or a polymer which was crosslinked to the extent of up to 6%, the crosslinks being polysulfide crosslinks or sulphydryl groups capable of forming crosslinks.

In addition to the use of Dimer acids in the preparation of polyesters for foam, Dimer acid has been reacted with ethylene oxide and the resulting polyol was converted into flexible foam. Densities ranged from 2 to 4 lb./ft.³ (190).

The utilization of foam scrap in urethane foams was described by König (96). The scrap was dissolved in either hot polyester and diisocyanate added or alternately dissolved in hot diisocyanate followed by polyester addition. Solutions of foam scrap in solvents boiling above 180°C. could also be utilized as additives for the production of polyester urethane foams.

Flexible urethane foam scrap was also reprocessed by dissolving it

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Edited by Dr. Günter Oertel

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Thus far polythioethers have remained commercially unimportant. They are prepared through the acid catalyzed condensation of thioglycol (prepared from hydrogen sulfide and ethylene oxide) alone or in a mixture with other diols [16].

Of more importance is the role of unsaturated polyols. Hydroxyl terminated homo- and copolymers of butadiene as well as ABS-polymers are used in the manufacture of polyurethane elastomers and caulking compounds. The unsaturation present permits reinforcement with carbon black and other fillers [17].

In the last 10 years, filled polyols have undergone considerable development particularly in the area of polymer polyols. Included under this heading are quite a number of graft copolymers. These have the common characteristic of containing finely divided dispersions of polymers which to some extent are chemically bound to the polyethers [18 to 20]. Next to polyurea dispersions (PHD-polyethers), vinyl modified polyether dispersions have made a substantial contribution to the improvement of many polyurethane products. Vinyl modified polyether dispersions are obtained through the in situ radical polymerization of olefinic monomers in polyethers. (For a more detailed description see subsection 3.3.1.1.)

3.1.1 Polyether

The manifold variations in commercial polyurethane chemistry is to a large extent due to the broad palette of commercially available starting materials coming from the polyethers and their modifications. "Polyethers" are understood here to be polyetherpolyols which are also called polyalkylene glycols or polyalkylene oxides. These are made by the reaction of epoxides (oxiranes) with active hydrogen containing starter compounds [11].

Polymerization products of this type have been known for quite a long time [21, 22]. By 1859 A. Wurtz had already obtained a small amount of polyethylene glycol when he completed the first ethylene oxide preparation. The state of the art of commercial polyether processing was not adequately developed at first and the products were not adequately standardized to permit consideration of these polyethers as intermediates to high polymers. They found increasing use though as lubricants, release agents, solubilizers, defoaming agents, and hydraulic fluids, as well as additives in the cosmetic and pharmaceutical industry. The particular suitability of the polyetherpolyols as a raw material in the manufacture of commercially interesting polyurethanes, especially foams, was first recognized in 1951 [23, 24].

The primary starting material for polyethers is 1,2-propylene oxide. Next to propylene oxide in importance is ethylene oxide which is often used with propylene oxide to make block copolymers. Pure polypropylene glycols are often utilized. On the other hand, because of their hydrophilic character, pure polyethylene glycols are seldom utilized. Another polyalkylene glycol which is also useful for reacting with isocyanates is obtained through the polymerization of tetrahydrofuran. Other less commonly used raw materials for polyethers will be mentioned in the following paragraphs.

Starters of very different types can be used in the poly-addition of epoxides in which primarily basic catalysis is used. Not only are the low molecular weight alcohols, phenols, amines, carboxylic acids, and water used as starter compounds but also the naturally occurring compounds such as cane sugar (sucrose), sugar alcohols (sorbitol, mannitol), as well as decomposition products from starch and cellulose. The di- and trifunctional alcohols as well as sucrose and sugar alcohols have established themselves as the most important commercial starting components. Diamines and amino alcohols are important starters in particular applications.

The functionality of the polyether is carried over from the functionality of the particular starting compound used. In the beginning stages of commercial development, when the manufacture of flexible foam was still being done through the prepolymer route, difunctional polyethers

POLYURETHANES *in* **Biomedical Applications**

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point. The two most commonly used isocyanates in polyurethane synthesis are toluene diisocyanate (TDI) and methylene bis (p-phenyl isocyanate) or 4,4'-diphenylmethane diisocyanate (MDI). TDI is less expensive than MDI, but MDI has superior reactivity, and polymers based on MDI may possess better physical properties. TDI is usually prepared as an isomeric mixture of 2,4-TDI and 2,6-TDI. MDI is crystallizable while 2,4-TDI does not crystallize in the solid state. Other aromatic diisocyanates, such as naphthalene diisocyanate (NDI) and 3,3' bitoluene diisocyanate (TODI) also can result in high-performance polymers, but at a higher cost than MDI based materials. Typical aliphatic isocyanates include 1,6-hexane diisocyanate (HDI), isophorone diisocyanate (IPDI), and methylene bis (p-cyclohexyl isocyanate) (H_{12} MDI). Because aromatic diisocyanates and polymers made from them are somewhat unstable toward light and become yellow with time, aliphatic isocyanates have found wider use in coating applications, than aromatic containing materials. In addition to greater light stability, polyurethanes based on aliphatic isocyanates possess increased resistance to hydrolysis and thermal degradation. Unfortunately, this is sometimes accompanied by a decrease in the mechanical properties of the material. The chemical structures of commonly used diisocyanates used in polyurethane synthesis are shown below, in Figure 14.

B. POLYOLS

Polyols available for elastomer synthesis include polyesters, polyethers, polycarbonates, hydrocarbons and polydimethylsiloxanes. The most commonly used polyols are polyether or polyester based compounds of molecular weight 400–5000. Primary alcohols will react readily with isocyanates at temperatures of 25–50°C. Secondary and tertiary alcohols are less reactive than primary alcohols by factors of 0.3 and 0.005 respectively. The flexible polyol comprises the soft segment matrix in which the hard segments are dispersed. Commonly used polyols are shown in Figure 15.

Traditionally, polyurethanes have been produced with polyester and polyether soft segments. Polyurethanes synthesized from polyesters possess relatively good physical properties; however, they are susceptible to hydrolytic cleavage of the ester linkage. Polyether-based polyurethanes exhibit a relatively high resistance to hydrolytic cleavage, when compared with polyester urethanes, and are favored for use in applications where hydrolytic stability is required. The polyether that results in a polyurethane with the best physical properties is polytetramethylene oxide (PTMO or PTMEG). Urethanes prepared with this soft segment show a level of mechanical strength comparable to that of polyester polyurethanes and possess relatively good hydrolytic stability and water resistance.²¹ Polyethylene oxide-based materials swell in water due to the hydrophilic nature of the soft segments. Polypropylene oxide-based polyurethanes offer greater hydrolytic resistance, but possess lower physical properties. When environmental stability is a major concern, polyalkyl glycols offer an alternative to the relatively less stable polyether and polyester polyurethanes.

Hydrogenated polybutadiene and polyisobutylene-based polyurethanes show excellent resistance to light and thermal degradation and hydrolysis.^{22,23} Unfortunately, the synthesis of these materials is difficult, and the physical properties of the resulting polymers are poor relative to those of conventional polyurethanes. The use of polydimethylsiloxane glycol (PDMS) as a soft segment leads to polyurethanes with improved low-temperature properties. The glass transition temperature of PDMS is about -123°C which allows the use of these materials at low temperatures.

C. CHAIN EXTENDERS

Chain extenders can be categorized into two general classes of aromatic diols and diamines, and the corresponding aliphatic diols and diamines. In general, aliphatic chain extenders yield softer materials than aromatic chain extenders. Commonly used chain extenders are shown in Figure 16. Chain extenders are used to extend the length of the hard segment, and increase the hydrogen-bond density and the molecular weight of the polyurethane. Trifunctional or higher chain extenders also act as branching or crosslinking agents. The reaction of equimolar quantities of macroglycol and

MACROMOLECULAR DESIGN OF POLYMERIC MATERIALS

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in some instances. Other less common dibasic acids, as well as other diols, have been employed including azelaic and sebacic acids and certain aromatic and cycloaliphatic diols.

In recent years, low-cost aromatic polyester polyols have been employed for the modification of both rigid urethane and isocyanurate foams. The major sources for these aromatic polyester polyols are residues from the dimethylterephthalate scrap (e.g., from PET bottles) and phthalic acid and its derivatives.

Unsaturated Polyesters Alkyd-type unsaturated polyesters were among the first polyols to be used in the preparation of rigid foams, as well as for the preparation of air-drying "uralkyd" or "urethane oils" type of coatings. Unsaturated polyester resins, after conversion into PU resins or combined with PUs, can be cross-linked with vinyl monomers such as styrene to find application in reinforced plastics applications (e.g., in combination with glass fibers).

Polyesters Derived from ϵ -Caprolactone (Polycaprolactones) These polyesters are prepared by ring opening polymerization of ϵ -caprolactone with glycols or triols to yield either difunctional or trifunctional hydroxyl-containing poly(caprolactone)s. These materials are of special interest in polyurethane elastomers, microcellular foams, coatings, and adhesives.

Hydroxyl-Terminated Polycarbonates Hydroxyl-terminated aliphatic polycarbonates produced from diols, such as 1,6-hexanediol or cycloaliphatic diols and phosgene, or by transesterification of carbonic acid diesters with a diol have been commercially available. These polyols have found applications in high-performance elastomers, coatings, and adhesives.

2. Polyethers

These polyols are the most widely used hydroxyl-terminated intermediates for flexible and rigid foams, elastomers, RIM, coatings, adhesives, sealants, and other urethane applications. The lowest cost polyether polyols are produced by anionic polymerization of alkylene oxides, primarily propylene and ethylene oxide, using diols, triols, or higher functional-based polyols for the oxyalkylation process. Since it is desirable to have hydrophobic properties for most urethane applications, propylene oxide is often used alone or in combination with ethylene oxide (generally less than 15%). The use of ethylene oxide, in general, is to provide terminal primary hydroxyl groups for faster reaction with the isocyanate groups. This is particularly important for fast demolding of foams or for RIM applications.

There are many ways of distributing the oxypropylene and oxyethylene groups in the formation of polyether polyols made from both propylene and ethylene oxide. The polymers can be random or block or combinations of both with either preponderantly terminal primary or secondary alcohol groups.

In the past, the preparation of high molecular weight polyols based on propylene oxide employing an alkali metal catalyst such as KOH was difficult due to the formation of terminal unsaturated groups. A new approach for producing high molecular weight polyether polyols with exceptionally low levels of unsaturation and exhibiting narrow molecular weight distribution was first developed by General Tire and later licensed by ARCO Chemical Co. (22-24). The preferred complex catalyst is a zinc hexacyanocobaltoate of the following formula:



Due to the absence of significant side reactions in the propoxylation step, the molecular weights of the resultant polyols are very close to the theoretical values. The polyols have exhibited better physical properties in elastomers and foams than conventional polyols of the same molecular weight due to the lower monol content.

Poly(oxyethylene) glycols (PEGs) are produced using only ethylene oxide in the oxyalkylation process. The resulting PEGs are used for the production of hydrophilic urethane polymers, including foams, and other urethane applications where high water absorption or controlled release of drugs, cosmetics, detergents, etc., are desired.

In addition to glycols as base polyols for the production of polyether polyols, triols (e.g., glycerol, trimethylolpropane, 1,2,6-hexanetriol), tetrols (pentaerythritol and α -methyl glucoside),

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